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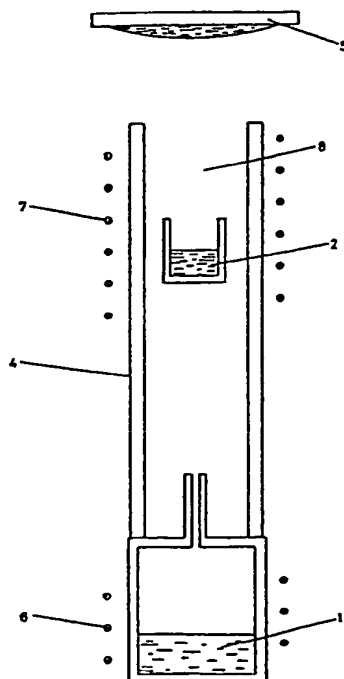
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(54) Multiple source physical vapour deposition.

(57) An improved apparatus for the physical vapour deposition of bulk alloys utilises at least two evaporation sources, each with means to maintain each evaporator at an independent temperature, communicating with a mixing chamber which has a single discharge outlet facing a temperature controlled collector, means being provided to heat the walls of the mixing chamber to a temperature at least as high as the hottest source to suppress condensation and to promote mixing of the respective vapour streams by scattering from the hot walls.

In a preferred arrangement as illustrated in Fig 1 sources 1, 2 are mounted vertically, one above the other, in a flue 4 heated by radiant heater 7. The flue radiates heat onto second source 2. The more volatile constituent is evaporated from lower source 1 by heater 6 and its vapour flows upwards past second source 2 into mixing zone 8. Here it mixes with vapour from source 2 and the mixture passes from the flue onto collector 5. The arrangement may be used for depositing binary magnesium alloys or zinc alloys.



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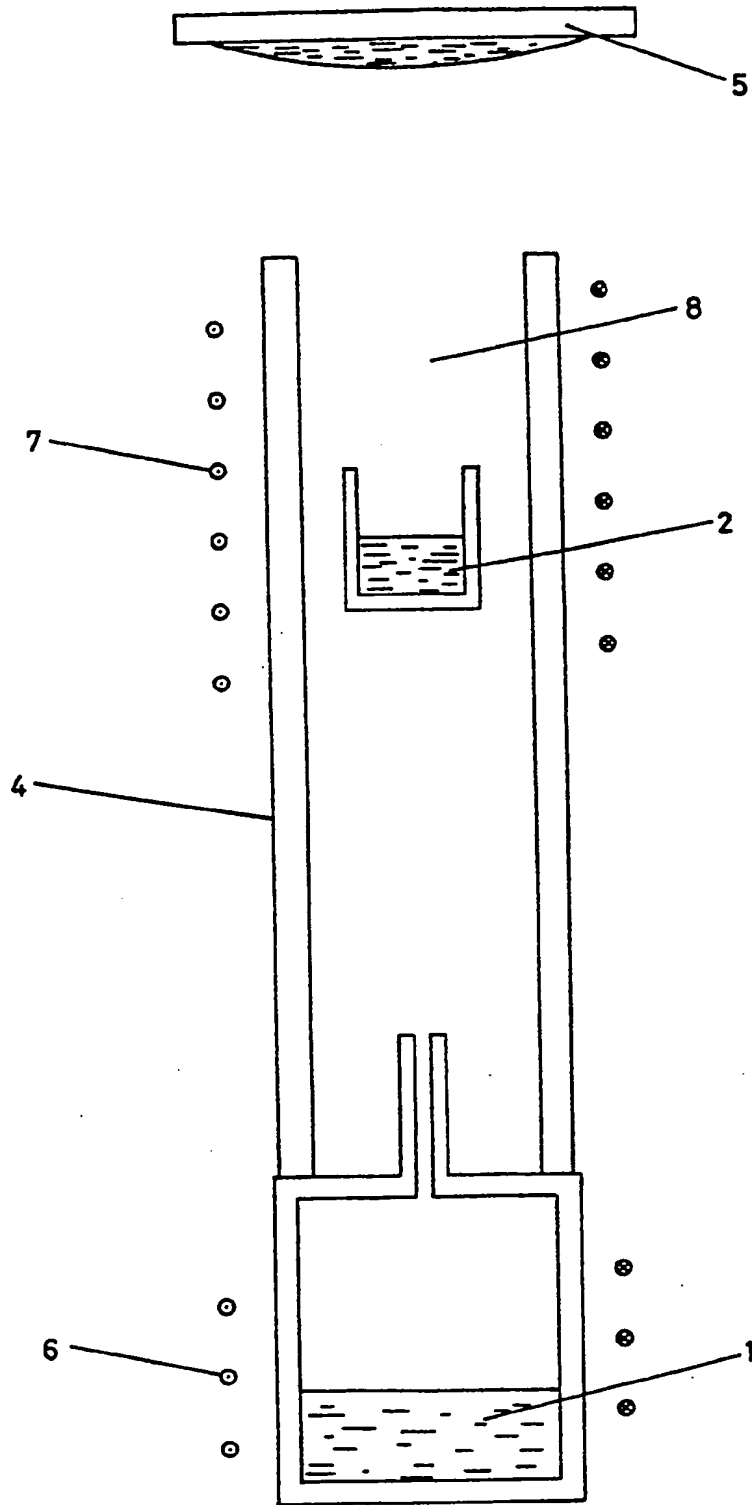


FIGURE 1

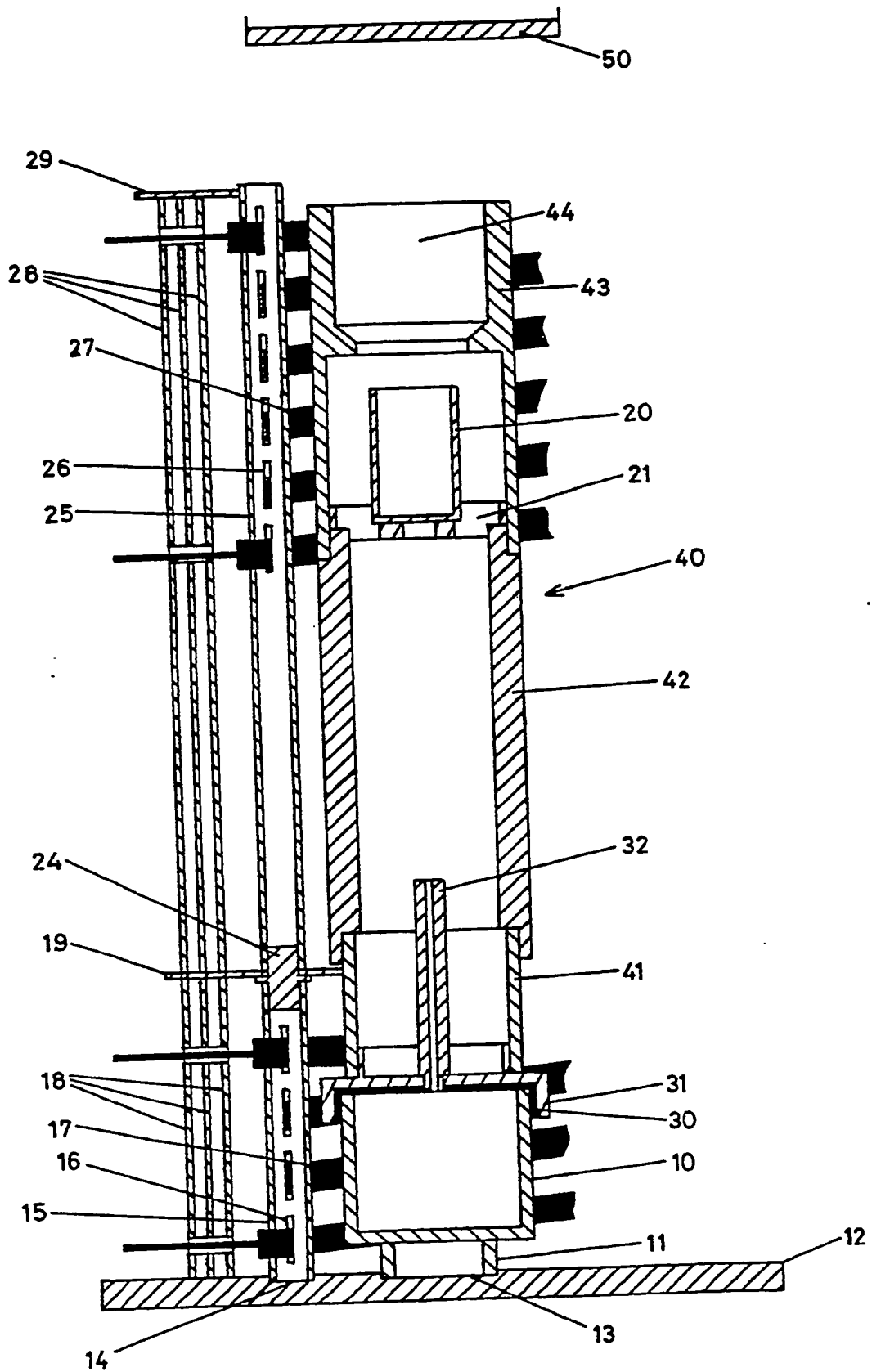


FIGURE 2

MULTIPLE SOURCE PHYSICAL VAPOUR DEPOSITION

This invention relates to improved apparatus and a method for the preparation of bulk alloys by a physical vapour deposition process of the type described in our earlier British Patents GB 1206 586 and GB 1265 965, in which alloy constituents are evaporated from one or
5 more evaporation baths and condensed upon a temperature controlled collector. The apparatus is operated under vacuum within a vacuum chamber. In the text which follows the phrase "physical vapour deposition" is to be interpreted as referring to the process outlined above.

10 Recently there has been growing interest in the possibility of obtaining improved magnesium alloys by creating new compositions achievable through rapid solidification rate (hereinafter referred to as RSR) production processes. Although magnesium is the lightest of the structural metals, its alloys have not found widespread use in
15 aerospace applications, partly because of certain shortcomings in mechanical properties, but principally because of their poor corrosion resistance. In magnesium alloys produced by conventional non-RSR methods, the addition of elements such as aluminium, chromium or silicon which are known to form protective surface films in other alloy
20 systems, is ineffective because of their insufficient solubilities in the magnesium matrix. Under normal equilibrium conditions, the concentration of such additives in solid solution is too low to provide an effective barrier to corrosion.

For the purpose of improving corrosion resistance it is very
25 important that the additives should be assimilated into a solid solution

with a uniform electrode potential. If they are allowed to segregate and form precipitates, and if the precipitates and matrix have different electrode potentials, then they effectively behave as tiny Galvanic cells and corrosion resistance is worsened rather than improved.

5 Rapid solidification and physical vapour deposition techniques provide the means to overcome thermodynamic constraints and achieve compositions which are beyond the scope of the ingot metallurgist by 'freezing' constituent atoms in position before they have the opportunity to migrate and segregate as they would in conventional melt chill
10 processes. These techniques therefore offer a potential solution for improving corrosion resistance in magnesium alloys by increasing the population of corrosion - inhibiting species in the magnesium matrix without forming harmful precipitates.

15 Physical vapour deposition has several advantages over RSR processing. Firstly, the cooling rate is higher, thereby improving the opportunity for forming solid solutions. Secondly, the choice of potential alloying constituents is considerably widened because whilst certain elements may not be miscible in the molten state, perhaps
20 because of phase differences, their vapours can be mixed intimately. This is particularly true in the case of magnesium because, at the melting temperature of many potentially interesting alloying additions, magnesium has a very high vapour pressure and will quickly evaporate away. Finally, consolidation of powder or flake associated with RSR
25 processing is avoided.

30 The preparation of magnesium alloys containing for example aluminium, chromium or silicon by the physical vapour deposition process poses special problems because of the large differences between the vapour pressure of magnesium and the vapour pressures of the additives. The patent specifications mentioned previously disclose that
35 alloy constituents can be evaporated either from a single evaporator or from separate evaporators. It is desirable to use a single evaporator whenever possible both for simplicity and to encourage a uniform composition in the deposit. However, when alloy constituents have vapour pressures which differ by several orders of magnitude, as in the magnesium-chromium system for example, this is no longer

practicable.

When separate sources are arranged side-by-side the composition of the deposit is non-uniform across the substrate due to imperfect mixing of the vapour streams. Better mixing can be achieved by increasing the separation of the collector from the sources but this has the effect of lowering the deposition rate.

One way of approaching this problem is to introduce lateral motion between the relative positions of the collector and the sources. In practice it is easier to keep the sources stationary and move the collector, either by rotation or by a reciprocating motion. In this way exposure of different parts of the substrate to the respective sources is equalized. Whilst a mobile collector offers considerable benefit in improving the homogeneity of the deposit, a small degree of local non-uniformity still arises because the deposit is effectively laid down as a series of sub-layers which are alternately rich in one particular constituent. In a structural member even this level of non-uniformity may be critical to its overall strength and could be bad for corrosion resistance.

Hitherto vapour deposition from multiple sources has either been a compromise between homogeneity in the deposit and the rate of deposition or has required special equipment to effect movement of the substrate relative to the position of the sources. This latter option is complicated by the need to maintain the apparatus under vacuum.

It is an aim of this invention to provide an apparatus and method which facilitates the deposition of homogeneous alloys at a high rate from multiple evaporation sources even when the constituent elements have widely differing vapour pressures.

The invention is an apparatus for use in a physical vapour deposition process (as previously defined) which comprises at least two evaporators with means to maintain each evaporator at an independent temperature, a temperature controlled collector, a vessel which embraces or communicates with the evaporators said vessel defining therewithin a vapour mixing chamber having a discharge opening facing the collector, and means to maintain the vessel walls in the part thereof delimiting the vapour mixing chamber at a temperature at least as high as the hotter

or hottest evaporator thereby to enhance mixing of the respective vapour streams whilst suppressing condensation of vapour on the chamber walls.

5 In a preferred form the apparatus comprises a vessel in the form of a rising flue or chimney with the evaporators positioned one above the other. At least the uppermost evaporator is positioned within the flue passage and the vapour mixing chamber is constituted by that portion of the flue passage which extends above the uppermost evaporator. In this arrangement the collector is horizontally disposed above the mouth
10 of the flue.

In another aspect the invention provides a method of physical vapour deposition (as previously defined) which comprises evaporating constituents from at least two evaporators maintained at independent temperatures, causing the constituent vapours to flow into a vessel
15 defining therewithin a vapour mixing chamber, heating the vessel walls in the part thereof delimiting the vapour mixing chamber to a temperature at least as high as the hotter or hottest evaporator thereby enhancing mixing of the respective constituent vapours by vapour reflection whilst suppressing condensation of vapour on the chamber
20 walls, and causing the mixed vapours to pass through a discharge opening in the vessel and impinge on a temperature controlled collector.

Clearly, for successful operation of the invention the walls of the vessel must be formed from a material inert to the metal vapours with
25 which they come into contact. The choice of material will therefore be determined by the nature of the metals to be evaporated.

The dimensions of the mixing chamber must be such that sufficient scattering occurs by reflection of vapour atoms from its hot walls to promote thorough mixing. If the mixing chamber is too large in relation
30 to the sizes of the respective sources and the flow rates of vapour therefrom, efficient mixing may not take place because the separation distance between the chamber walls and the sources is too great for sufficient scattering to occur.

Conveniently the constituent evaporated from the lowermost
35 evaporator is the most volatile and is also the principal alloy

constituent. Difficulties arising from unwanted condensation of vapour in undesired parts of the apparatus and reverse flow of vapour streams in the cooler regions are thus minimised.

Advantageously the flue is constructed in a number of longitudinal sections. This not only simplifies assembly of the apparatus between each operation by allowing easier access to the evaporator or evaporators within the flue passage, but also facilitates use of different materials in the different sections. For example, the lowermost section can be formed from a thermally insulating material to minimize conduction of heat downwards from the hottest regions of the apparatus to the lowermost evaporator. This is especially important when the lowermost evaporator contains a source of material which is particularly volatile.

Although the inventors know of no theoretical reasons why the evaporation sources cannot be mounted side-by-side using an arrangement of passages or nozzles to direct their vapour flows to a common mixing chamber, practical considerations favour the vertical configuration. Firstly, the general direction of vapour flow is inherently upward by virtue of the fact that the vapour evolves from a molten metal bath. To divert the flow from this generally upward path requires the intervention of guide means which would need to be heated to a temperature at least as high as the hottest evaporator, for the reasons given above. Thus extra energy is expended in keeping additional components hot. Secondly, because the vertical configuration is the most compact it can be accommodated in a smaller vacuum chamber.

Another advantage of the invention compared to known physical vapour deposition apparatus is that the deposited alloy has a more uniform composition across the substrate without recourse to undesirably low rates of deposition or to translation of the collector across the field of deposition. The equipment has the capability to produce homogenous alloys at a deposition rate of several millimetres per hour or even higher. The drawback of using very high rates of deposition is the occurrence of an unacceptable degree of porosity in the product so in practice the rate is optimised to achieve a sensible

microstructure.

By careful control of the vapour flow rates from the respective evaporators it is possible to deposit many constituents with wide differences between their vapour pressures.

5 The invention will now be described by way of example with reference to the following drawings, in which:

Figure 1 is a schematic diagram of the apparatus, and

10 Figure 2 is a vertical section through a preferred form of the apparatus with some detail omitted from the right hand side for clarity.

Referring now to Figure 1, reference numeral 1 denotes a lower evaporation source positioned at the bottom of a chimney 4 within which there is disposed a second evaporation source 2. Facing the mouth of chimney 4 is a collector 5 which receives the mixed vapours emanating
15 therefrom. Sources 1 and 2 each have an associated heater 6, 7. The lower heater 6 operates directly to heat the walls of a crucible which houses the lower evaporation source 1 whilst the second heater 7 operates to heat up the walls of the chimney which in turn radiates heat to the second evaporation source 2. Thus vapour is generated from the
20 second source whilst satisfying the condition that the chimney walls should be at least as hot as the hottest source.

Vapour from source 1 is supplied to the chimney 4 and flows past source 2 into a mixing zone 8 where it mixes with vapour from source 2. The mixing zone is simply that portion of the chimney above source 2
25 where both species of vapour coexist. Collisions between vapour stream 1 and the walls of the chimney or the second source 2 act so as to randomize movement of the vapour atoms and this assists thorough mixing with the vapour from source 2. Similarly, collisions between the vapour stream from source 2 and the walls of the chimney encourage
30 intimate mixing by imparting random movement to the vapour atoms. The mixed vapour stream emerging from the mouth of the chimney is therefore substantially homogeneous and a deposit with uniform microstructure is formed on the collector 5.

Figure 2 shows a preferred form of the apparatus in vertical
35 section with detail omitted from the right hand side for clarity. The

ed here has been developed particularly for the cesium alloyed with lower vapour pressure as aluminium, chromium or silicon. The evaporator comprises a mild steel crucible 10 standing on a support ring 11 which acts so as to minimize conduction of heat from the crucible to support table 12. The crucible is sealed with a screw-top lid 31, both made from mild steel. The gasket of the lid and gasket assembly is a graphite gasket the purpose of which is to control the flow of magnesium from the lower crucible.

The upper crucible and crucible lid are optional features which may be used for separating certain elements from the lower crucible. Experiments with magnesium, for example, had demonstrated the presence of an oxide layer on the molten metal surface which hindered the evaporation of the metal. When the oxide was present the evaporation rate was appreciably low. Increasing the temperature had little effect until the oxide was reached when the oxide was dispersed to the surface of the crucible, leaving a clean pool of molten metal in the crucible. At this temperature the evaporation rate was too high. This was eventually overcome by operating the lower evaporator at a temperature sufficiently high that the magnesium surface was clear of oxide. By positioning a nozzle at the mouth of the source to reduce the evaporation to the desired level. The required evaporation temperature for magnesium is in the range 700-800°C. The support table 12 is recessed at 13 and 14 to provide positive support for the support ring 11 and lower heater support 15. The lower heater support 15 is an alumina tube having slots through which are threaded heater element 17. The heater element comprises a single strip of tantalum metal wound in the form of a helix around the lower crucible 10. To reduce radiation losses the heater is protected by three stainless steel screens 18. Molybdenum is placed over the crucible and screens to reduce the radiation lost from the top heater 27 down to the mild steel

passing through the nozzle 32 the vapour enters vertical

chimney 40 which, in practice, is formed in three sections. Lower section 41 is made from alumina which has a poor thermal conductivity and therefore helps to insulate the first evaporation source from the higher temperatures prevailing at the second evaporation source. The middle section 42 and top section 43 are formed of graphite for reasons which will become apparent below.

Crucible 20 holding the second evaporation source is located at the junction between the middle section 42 and the top section 43 of the chimney. It rests on a graphite support ring 21 which contains a number of holes to facilitate passage of magnesium vapour from the lower source past the crucible 20 into the top section of the chimney. The top section of the chimney defines a mixing zone 44. Here the vapour from the lower source mixes with vapour from the second source before flowing out of the chimney and condensing on a temperature controlled collector 50.

Different materials may be employed for the crucible 20 depending on the material to be evaporated. An alumina crucible is suitable for the evaporation of aluminium or chromium, whereas a vitreous carbon crucible is used for the evaporation of silicon.

A second radiant heater 27 is used to heat the chimney in the vicinity of the second evaporation source. Heat radiated from the chimney is then used in turn to heat the second evaporation source to generate vapour therefrom. Successful operation of the invention depends on maintaining the temperature of the chimney at least as high as that of the second evaporator otherwise vapour condenses on the chimney walls. These difficulties are conveniently overcome by using the arrangement outlined here where a radiant heat source is used to heat the chimney which then radiates heat onto the crucible 20.

The reasons for choosing graphite as the material for the middle and top sections of the chimney are two-fold: Firstly, graphite has a high thermal conductivity and a high emissivity which allows rapid transfer of heat to the inside wall of the chimney and thence to the crucible 20 by radiation. Secondly, graphite is physically and chemically stable up to 3000°C in vacuum and can be easily machined to shape.

The upper heater 27 is also a single tantalum strip wound in a helix

through slots 26 in tubular alumina heater supports 25. These upper heater supports are coupled to their lower counterparts 15 through the agency of spigots 24 which protrude through the molybdenum disc 19. The spigots 24 are dimensioned to be a loose fit in the bores of the alumina tubes.

The operating temperature of the second evaporator will obviously depend on the material being evaporated. For example, aluminium and chromium require a temperature of 1300°C to achieve a satisfactory evaporation rate whilst silicon requires a temperature of about 1550°C. This figure represents the maximum feasible operating temperature of the apparatus as described because at higher temperatures the tantalum was susceptible to chemical interaction with the support material. By using a different combination of heater and support material the operating temperature range may be extended.

Since the chimney is much hotter in operation than the mild steel crucible 10, more radiation screens 28 are provided to surround it, the number of screens required being dependent on the evaporation temperature of the second source. In practice, nine screens are used for the evaporation of chromium whilst twelve screens are required for silicon. The three inner screens are made from molybdenum which does not melt until 2610°C and has a very low vapour pressure. The remaining screens are shielded from the heat source to be sufficiently cool to be formed from stainless steel without danger of contamination of the deposit.

Finally, five horizontally-disposed annular screens of molybdenum 29 are placed over the screens 28 to cover the heater 27 and shield the collector 50 from excessive radiant heating, without restricting the flow of vapour. Only one screen 29 is shown for clarity.

Although the apparatus has been particularly described with reference to the deposition of binary magnesium alloys, it is equally well suited to other alloy systems where one of the major constituents has a much higher vapour pressure than the other alloying ingredients, such as zinc alloys. It is also envisaged that more than two evaporation sources could issue into a common mixing chamber. One means of accomplishing this would be to sustain a temperature gradient in the

middle section of the chimney by differential heating which increases towards its mouth and to provide intermediate supports capable of supporting a third or further crucibles. Many other modifications will be apparent to those skilled in the art without departing from the scope
5 of the following claims.

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CLAIMS

1. Apparatus for use in a physical vapour deposition process (as previously defined) which comprises at least two evaporators with means to maintain each evaporator at an independent temperature, a temperature controlled collector, a vessel which embraces or communicates with the evaporators said vessel defining therewithin a vapour mixing chamber having a discharge opening facing the collector, and means to maintain the vessel walls in the part thereof delimiting the vapour mixing chamber at a temperature at least as high as the hotter or hottest evaporator thereby to enhance mixing of the respective vapour streams whilst suppressing condensation of vapour on the chamber walls.
2. Apparatus as claimed in claim 1 comprising a vessel in the form of a rising flue with the evaporators positioned one above the other, wherein at least the uppermost evaporator is positioned within the flue passage and the vapour mixing chamber is constituted by that portion of the flue passage which extends above the uppermost evaporator and wherein the collector is horizontally disposed above the mouth of the flue.
3. Apparatus as claimed in claim 2 wherein the lowermost evaporator comprises a heated crucible having a nozzle to control the flow rate of vapour emanating therefrom.
4. Apparatus as claimed in claim 2 or claim 3 wherein the flue is constructed in longitudinal sections to facilitate access to the evaporator or evaporators within the flue passage and wherein the lowermost section of the flue is formed from a thermally insulating material to minimize conduction of heat downwards from the hottest regions of the apparatus to the lowermost evaporator.
5. A method of physical vapour deposition (as previously defined) which comprises evaporating constituents from at least two evaporators maintained at independent temperatures, causing the constituent

maintained at independent temperatures, causing the constituent vapours to flow into a vessel defining therewithin a vapour mixing chamber, heating the vessel walls in the part thereof delimiting the vapour mixing chamber to a temperature at least as high as the hotter or hottest evaporator thereby enhancing mixing of the respective constituent vapours by vapour reflection whilst suppressing condensation of vapour on the chamber walls, and causing the mixed vapours to pass through a discharge opening in the vessel and impinge on a temperature controlled collector.

6. A method as claimed in claim 5 which comprises evaporating the constituents from evaporators positioned one above the other with at least the uppermost evaporator located within the heated passage of a rising flue, and causing the constituent vapours to mix in that portion of the flue passage which extends above the uppermost evaporator.

7. A method as claimed in claim 6 which comprises evaporating the most volatile constituent from the lowermost evaporator.

8. Apparatus for use in a physical vapour deposition process as claimed in claim 1 and substantially as hereinbefore described with reference to Figures 1 and 2 of the accompanying drawings.

9. A method of physical vapour deposition as claimed in claim 5 substantially as hereinbefore described with reference to Figures 1 and 2 of the accompanying drawings.